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PATENT

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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicant: KI UGE et al

Examiner: BERNES, D.J

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For: Nitrogen Oxide Storage Material and nitrogen Oxide Storage Catalyst  
Produced Therefrom

Customer No.: 23719

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Commissioner for Patents  
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March 1<sup>st</sup>, 2010

**DECLARATION OF DR MEIKE WITTROCK**

**UNDER 37 C.F.R. § 1.132**

1. I, Meike Wittrock, hereby declare that:
2. I am co-inventor of the above application and I am an expert in the areas of nitrogen oxide storage catalysts and catalytically active coatings
3. I received my diploma in Chemistry from Friedrich-Schiller-University Jena / Germany in 1998 and my Ph D. in Natural Sciences (Dr. rer. nat.) in 1999 from the University of Cologne / Germany. I have worked extensively for 6 years in the development of catalytically active coatings of heterogeneous catalysts for gas purification processes and methods of applying them to carriers and thereof 3.5 years especially on nitrogen oxide storage catalysts
4. I submit this declaration based upon: (i) my training, knowledge, education, and experience in chemistry, notably in the fields of nitrogen oxide storage catalysts and catalytically active coatings and methods of applying them to carriers; (ii) my review of the above-referenced application and the history of the prosecution of this application; and (iii) my review of the prior art cited by the Examiner during prosecution of this application including U.S. Patent No. 6,858,193 and US

2003/0125202 , collectively referred to as ("Ruwisch") and US 6,350,421 (Strehlau).

5. I disagree with the Examiner's opinion discussed in the Final Office Action of 4 December 2009 that Ruwisch and Strehlau make our invention obvious.
6. From my reading of the Ruwisch and Strehlau references, they do not make obvious the unexpected thermal durability that we discovered when we used the oxidation-active component (Pt) on a first support material of homogeneous Mg/Al oxide and used the NOx storage component (BaO) on a second support material also containing homogeneous Mg/Al oxide. Therefore, our patent application is an improvement over the Ruwisch and Strehlau references.
7. Table 3 of our patent application shows the coating compositions that we tested. Each coating composition was composed of the coating components listed:

TABLE 3

Composition of the catalysts					
Coating components	Support	Catalytically active components			
	material [g/l]	Platinum [g/l]	Palladium [g/l]	Rh [g/l]	BaO [g/l]
<u>Catalyst C1</u>					
→ Pt/CeO <sub>2</sub> /Mg—Al oxide	102.8	3.18			
BaO/CeO <sub>2</sub> /Mg—Al oxide	126.3				25.3
<u>Catalyst C2</u>					
Pt/BaO/CeO <sub>2</sub> /Mg—Al oxide	102.8	3.18			25.3
Ce—Zr oxide	126.3				
<u>Comparative catalyst CC1</u>					
Pt/CeO <sub>2</sub> /Mg—Al oxide	102.8	3.18			
BaO/Ce—Zr oxide	126.3				25.3
<u>Catalyst C3</u>					
→ Pd[Pt/CeO <sub>2</sub> /Mg—Al oxide]	102.8	3.18	1.06		
BaO/CeO <sub>2</sub> /Mg—Al oxide	126.3				25.3
Rh/Al oxide	10.0			0.35	
<u>Comparative catalyst CC2</u>					
Pd[Pt/CeO <sub>2</sub> /Mg—Al oxide]	102.8	3.18	1.06		
BaO/(Mg—Al oxide + Ce—Zr oxide)					25.3
Rh/Al oxide	10.0			0.35	
<u>Comparative catalyst CC3</u>					
Pd[Pt/BaO/CeO <sub>2</sub> /Mg—Al oxide]	102.8	3.18	1.06		
BaO/(Mg—Al oxide + CeO <sub>2</sub> )					25.3
Rh/Al oxide	10.0			0.35	
<u>Catalyst C4</u>					
Pd[Pt/BaO/CeO <sub>2</sub> /Mg—Al oxide]	102.8	3.18	1.06		25.3
Ce—Zr oxide	126.3				
Rh/Al oxide	10.0			0.35	
<u>Catalyst C5</u>					
→ Pd[Pt/CeO <sub>2</sub> /Mg—Al oxide]	102.8	3.18	1.06		
BaO/CeO <sub>2</sub> /Mg—Al oxide	126.3				25.3
Ce—Zr oxide	126.3				
Rh/Al oxide	10.0			0.35	
<u>Comparative catalyst CC4</u>					
Pt/CeO <sub>2</sub> /Mg—Al oxide	102.8	3.18	1.06		
BaO/Ce—Zr oxide	126.3				25.3
Rh/Al oxide	10.0			0.35	

8. From Table 3, the nitrogen oxide storage catalysts C1, C3 and C5 have as the oxidation component Pt, which is supported on a first support material containing homogeneous Mg/Al oxide and as the nitrogen oxide storage component BaO, which is supported on a second support material also containing homogeneous Mg/Al oxide. These (support) materials are separate powder components.
9. We compared our catalysts C1 (containing first and second support material containing homogeneous Mg/Al oxide) to a comparative catalyst CC1 that had a first support material containing homogeneous Mg/Al oxide, but did not have the nitrogen oxide storage material containing BaO as the nitrogen oxide storage component supported on a second support material containing homogeneous Mg/Al oxide. The nitrogen oxide storage material in CC1 was composed of BaO as the nitrogen oxide storage component and Ce-Zr oxide as the second support oxide. The NO<sub>x</sub> storage efficiency after ageing of the catalysts (synthetic so-called "rapid" ageing by storing the catalysts at 850°C in air for 24 h) are shown graphically in Figure 3.

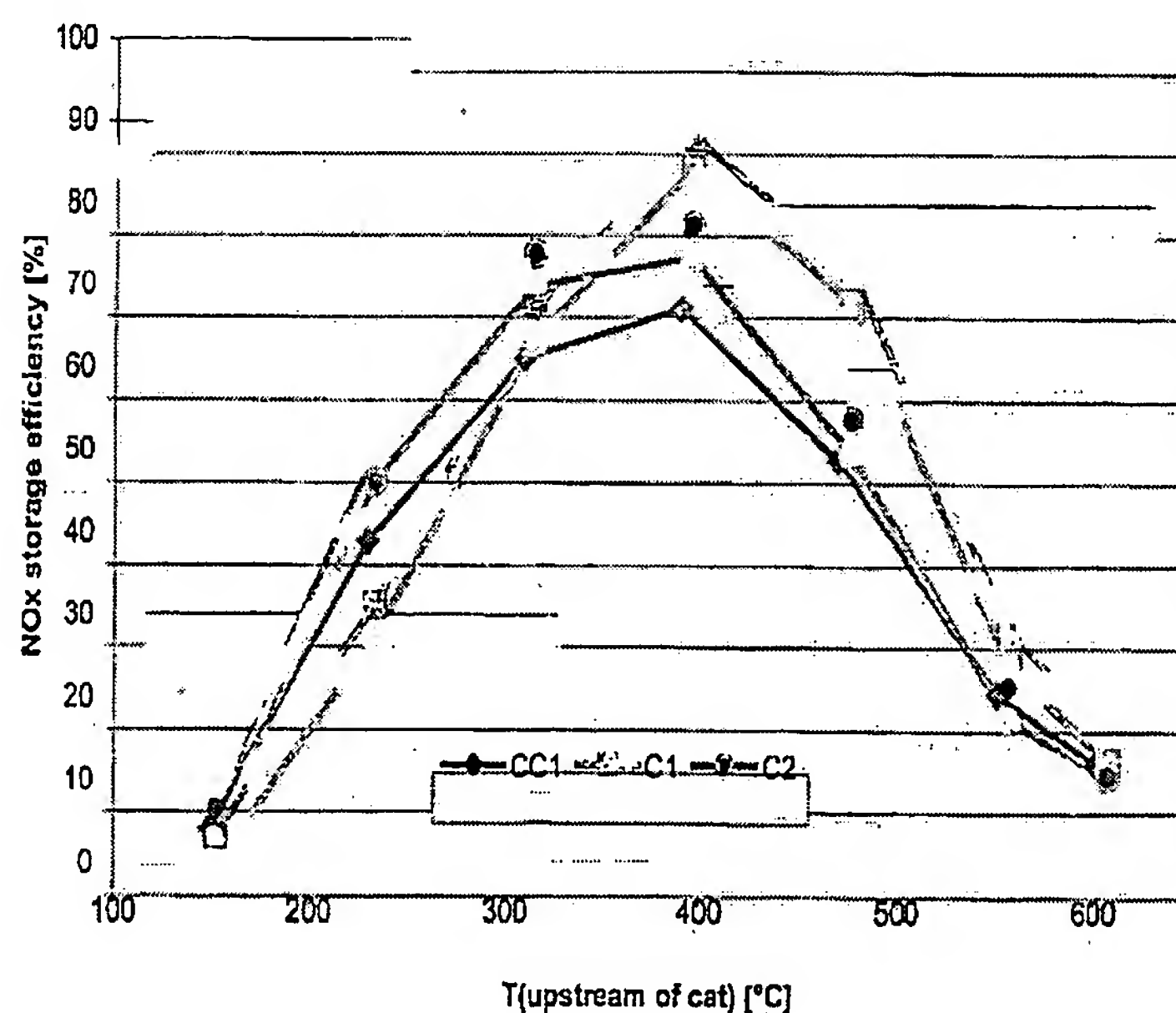


Figure 3

10. As can be seen from Figure 3, the C1 catalyst had improved thermal durability and NO<sub>x</sub> storage efficiency at high temperatures (above 350°C) compared to the catalyst CC1. This was unexpected

11. We also compared our catalysts C3 and C5 (containing first and second support material containing homogeneous Mg/Al oxide) to a comparative catalyst CC4 that had a first support material containing homogeneous Mg/Al oxide, but did not have the nitrogen oxide storage material containing BaO as the nitrogen oxide storage component supported on a second support material containing homogeneous Mg/Al oxide. In CC4 the nitrogen oxide storage component BaO was supported on Ce-Zr oxide as the second support material. The results are shown graphically in Figure 5.

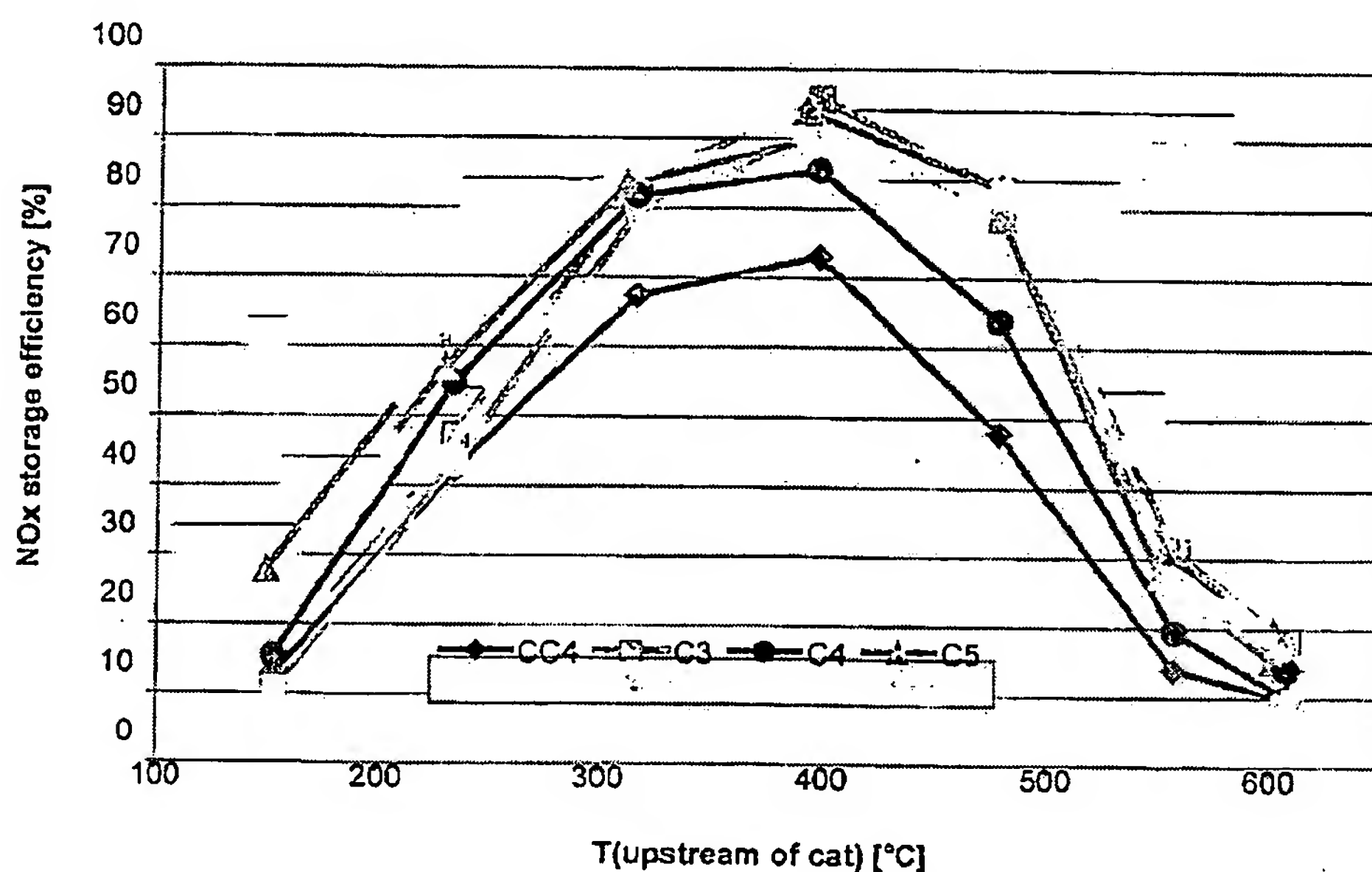


Figure 5

12. As you can see from Figure 5, the C3 and C5 catalysts had improved thermal durability and NOx storage efficiency at temperatures above 300°C compared to the catalyst CC4 that does not have a second support material containing homogeneous Mg/Al oxide. Especially the comparison of C3 and CC4 shows the influence of the use of homogeneous Mg/Al mixed oxide as a second support oxide used in the NOx storage material. The results we saw were unexpected. We did not expect there to be such a great improvement in NOx storage efficiency after ageing and hence in thermal stability at temperatures above 300°C.
13. With regard to Ruwisch, I believe that our invention is an improvement over Ruwisch. For my reading Ruwisch lists homogeneous Mg/Al oxide as a support material for the oxidation component containing Pt, but Ruwisch does not suggest using Mg/Al oxide as a second support material for the nitrogen oxide storage

component, as we do. Ruwisch suggests in [0043] to use the Mg/Al mixed oxide “in combination with the nitrogen oxide storage material of the catalyst” The term “nitrogen oxide storage material” has to be distinguished from the term “nitrogen oxide storage component” Ruwisch gives a definition of both in [0036] From that it is clear, that the nitrogen oxide storage component (e.g. BaO) shall be supported on a suitable support material in a highly dispersed form. In [0048] several suitable support materials are nominated, but in fact Ruwisch uses only Ce/Zr oxide. All catalysts specifically disclosed in Ruwisch contain BaO/Ce/Zr oxide as nitrogen oxide storage material, see Table 3. Furthermore Ruwisch teaches in [0043], that the Mg/Al mixed oxide shall serve as a support material for the precious metal compound (PGM). It can be seen from Table 3, that all catalysts shown in Ruwisch contain at least two powders. At least one powder which comprises the PGM on a support oxide and in addition the nitrogen oxide storage material BaO/Ce/Zr oxide as a separate powder. I understood from the disclosure of Ruwisch that the term “to use the Mg/Al mixed oxide “in combination with the nitrogen oxide storage material of the catalyst”” advises to combine at least two powders: PGM on Mg/Al mixed oxide and a (standard) nitrogen oxide storage material.

14. Comparative example CC2 as disclosed in Ruwisch. Table 3 (catalyst CC2) lists Mg/Al oxide as a first support material for the oxidation component containing Pt in combination with pure Mg/Al mixed oxide. I did not understand this as the recommendation to use two separate support materials containing Mg/Al oxide for the oxidation component and the nitrogen oxide storage component as we do, quite the contrary. [0079] explains, that the pure Mg/Al mixed oxide was used in CC2 instead of the nitrogen oxide storage material BaO/Ce/Zr oxide. Ruwisch shows in figure 3, that this catalyst has become completely unsuitable for nitrogen oxide storage after ageing. This example shows, that the Mg/Al mixed oxide is unsuitable as nitrogen oxide storage material. From this I understood that the Mg/Al mixed oxide would not contribute to the nitrogen oxide storage efficiency.
15. Therefore I was surprised to find significantly improved thermal durability and NOx storage efficiency at temperatures above 300°C that we discovered using a first and second support material of Mg/Al mixed oxide, whereby the first one was used to support the oxidation component and the second one was used to support the nitrogen oxide storage component.  
Ruwisch does not make obvious the unexpectedly improved thermal durability and NOx storage efficiency at temperatures above 300°C that we discovered using a first and second support material of Mg/Al mixed oxide.
16. With regard to Strehlau, this reference describes different nitrogen oxide storage materials including e.g. BaO as nitrogen oxide storage component loaded on a



high surface area support material. Depending on this support material Strehlau distinguishes four groups of nitrogen oxide storage materials, whereby the first group includes support materials based on cerium oxide (as used in Ruwisch) and whereby the second group includes stoichiometrically composed mixed oxides (alkaline earth titanate, barium stannate and barium zirconate, but no aluminates; see col. 5, lines 8 – 27)). Due to my understanding Strehlau teaches, that for use as nitrogen oxide storage materials loading the support material with 10 wt.-% to 45 wt.-% of the storage components with respect to the total weight of storage material is desirable (col. 5, lines 60 – 64).

Furtheron Strehlau points out, that care must be exercised that the chosen material pair support oxide / storage component does not tend to form mixed oxides (see col. 8, lines 57 – 59). Table 1 shows, that Mg spinel which contains 31 wt.-% MgO and 69 wt.-%  $\text{Al}_2\text{O}_3$  when used as support material in combination with the storage component BaO produces  $\text{BaAl}_2\text{O}_4$ . According to my experience such a formation of mixed oxides of the nitrogen oxide storage component and its support material causes a loss of NOx storage efficiency after thermal ageing. In addition it is disclosed in col. 10, lines 59 – 64, that MgO in  $\text{MgAl}_2\text{O}_4$  does not form a mixed oxide with barium oxide. In view of this disclosure I would have expected that the use of a Mg/Al mixed oxide containing 1 to 30 wt.-% MgO as a support material for the nitrogen oxide storage component would cause a loss of thermal durability.

Strehlau does not disclose the unexpected thermal durability that we discovered when we used the oxidation-active component on a first support material of homogeneous Mg/Al oxide and used the NOx storage component on a second support material also containing homogeneous Mg/Al oxide. Therefore, Strehlau does not make the claims obvious.

17. In my opinion, the references cited by the Examiner Ruwisch and Strehlau do not make our invention obvious as they do not show the unexpected thermal durability that we discovered when we used the oxidation-active component on a first support material of homogeneous Mg/Al oxide and used the NOx storage component on a second support material also containing homogeneous Mg/Al oxide
18. All statements made herein of my own knowledge are true, and all statements made on information and belief are believed to be true. All statements are made with the knowledge that willful, false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

  
Dr. Meike Wittrock

March 2<sup>nd</sup>, 2010  
Date